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## COMPLETE SPECIFICATION

### Modified Synthetic Condensation Polymers and their production

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to modified synthetic condensation polymers and their production.

Many types of synthetic condensation polymers are known and have been successfully used in the preparation of shaped articles, particularly for the production of artificial textile materials and films. Examples of such condensation polymers are polyamides, polyesters, polyethers, polyureas, phenoplasts, aminoplasts and polyurethanes. Most of these materials have some outstanding property or combination of properties which renders them especially suitable for some particular end use. Obviously, no one polymer or group of polymers is best for all purposes. However, no matter how suitable a material may be for a given application, almost invariably it is deficient in some respect. For example, where high hardness is required, the material may be brittle and lack good impact strength, or if a fibre of good elasticity is wanted, the candidate with best elasticity may have too low a melting point. Polymeric materials which form films of good strength and transparency may be deficient in dielectric properties or may be permeable to reagents which it is desirable to exclude. Fibres which have good strength, elasticity, and modulus and which can be woven into attractive fabrics may be very difficult to dye.

In the past, some of these deficiencies have been partially corrected by the use of inert fillers, by the addition to the monomer or monomers from which the polymer is made of a further monomer or monomers to form a

copolymer, or by the use of a coating agent applied to the surface of the shaped article. All these expedients have their attendant disadvantages. The use of an inert filler may impair the appearance or transparency of a product, or the filler may be susceptible to degradation in an environment to which the matrix material is resistant. A copolymer often will have poorer properties than those of either component alone, so that it might become necessary for example to sacrifice the high melting point of a pure component for the lower melting point of a copolymer which had acceptable dyeability.

The use of coatings would appear to offer large advantages when the object is to modify surface characteristics of the shaped article. Modifications of this kind which have often been attempted in the past relate to improved anistatic properties, wettability, soil repellency, ease and permanence of dyeing or printing, vapour permeability, hand, warmth and innumerable other properties. However, such treatments are obviously effective only as long as the coatings are retained during use. A common problem has been that thin coatings are not sufficiently resistant to use, while thick coatings, which may be more resistant or self-supporting, often spoil the appearance or handle of the treated article, making it unacceptable to the consumer.

The present invention comprises graft copolymers in which the substrate is a synthetic condensation polymer and the grafted structures at least in part contain free carboxyl groups or carboxylate salt groups and are derived from monomers containing reactive non-aromatic carbon-carbon unsaturation. Graft copolymers in which the grafted structures contain carboxylate salt groups in which the salt-forming component is a metal are particularly useful.

These graft copolymers can be obtained by subjecting the synthetic condensation polymer to ionising radiation while it is in intimate

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contact with the corresponding unsaturated acid or an anhydride, half-acid ester or half-acid amide thereof, or a derivative and that can be, and subsequently is, hydrolysed to the acid, e.g. the corresponding acid chloride; when a salt is desired the product is subsequently subjected to the action of a solution containing a basic-reacting metal or other salt. For the sake of brevity the unsaturated acid or derivative thereof will be referred to as the "modifier." In the present specification and claim grafted structures actually obtained from any of these monomers are regarded as being "derived" from the corresponding unsaturated acid.

In a particularly valuable application of the invention the copolymer is treated in the form of a shaped article, especially a textile article or film.

The modifier may be dispersed in the condensation polymer before the irradiation or, when it is desired to modify only the surface of a shaped article, it may be applied to the exterior of the article, e.g. as a solution or in suitable cases as a pure compound, for instance by spraying, calendering, immersion, padding, or exposure to vapour condensation. In suitable cases a solution of the modifier may be applied to the surface of a shaped article and the solvent flashed off before the irradiation. If desired excess liquid may be removed before irradiation as by squeezing. When the modifier is applied to the exterior of a shaped article it is preferable to use high energy particle radiation. When shaped articles which are relatively thin in at least one dimension, e.g. films, fibres, or fabrics, are treated, a great number of layers of the material can be simultaneously subjected to the irradiation, the necessary penetration then being achieved by the use of X-rays or gamma rays of short wave length.

It is often of advantage to keep the polymer or article out of contact with oxygen or moisture while it is irradiated. For instance it may be in an inert gas, or enclosed in a material which is substantially impervious to air and water such as polyethylene film or aluminium foil, so limiting the amount of air or water in contact with the polymer. Instead of or as well as this there may be present a compound which has a protective or antioxidant effect, e.g. cysteine, carbon, or a polyethylene glycol, which will prevent or reduce degradation of the modifier and/or the substrate. The effect of the irradiation can sometimes be considerably increased by the presence of materials which convert the radiation absorbed into a more effective form which they subsequently release to the material. Compounds with this property are somewhat similar to sensitizers in photography, except that in this case useful materials absorb high energy radiation and emit the energy in a lower and more usable range. Phosphor screen containing calcium tungstate, zinc sulphide or metallic lead or the like are

useful for this purpose. The phosphor materials may be used as plates contacting the material being treated, or may be incorporated in the modifying agent or even be coated on or dispersed in the organic polymer which it is desired to modify.

The irradiation may be accomplished over a wide range of temperatures. However, a low temperature decreases the tendency toward oxidation or thermal degradation. Since the absorption of particle radiation frequently causes a temperature increase in the range of about 2°C. for each Mrep absorbed, if high tube current is employed so that absorption is complete within a short time interval, it is usually advisable to provide means to remove the heat generated to avoid injury to the sample. The use of solid carbon dioxide to maintain a cold atmosphere is very satisfactory for this purpose. In general, irradiation at a higher temperature promotes the speed with which bonding occurs, thus making possible a higher throughput from a given piece of equipment at a constant radiation dosage. Temperatures as low as -80°C. and as high as 150°C. may be employed, but it is usually preferred to keep the temperature of the polymer within the range 0° to 75°C.

The unsaturated acid or acid derivative employed is preferably of relatively low molecular weight, since it is desirable that the acids penetrate into the polymer or shaped article, and low molecular weight acids do this more readily. Thus ethylenically unsaturated acids with up to 5 carbon atoms are preferred, though acids with as many as 20 carbons in chain length may be used. For maximum activation of the double bond it is desirable that it be in close proximity to the carboxyl group, and this also appears to enhance the rate of penetration. Suitable unsaturated acids include crotonic, furoic, acrylic, maleic, dichloromaleic, fumaric and itaconic acids. The unsaturated acid may contain substituent groups which it may be desirable to attach to the polymer to confer other properties, such as static reduction or moisture repellance.

After the unsaturated acid has become attached to the substrate, a metal salt of the acid is formed by subjecting the irradiated composition or article to the action of a solution containing a basic metallic salt. Any positively charged metal ion from a basic-reacting salt can be attached to the grafted acid. It is merely necessary that the anion of the said metal salt be a somewhat weaker acid than the grafted unsaturated acid. In general the greater this difference in acid strength, the greater is the amount of the metal ion taken up under constant conditions, e.g. irradiation dose, concentration and temperature. It is preferable that the dissociation constant of the anion acid be no greater than about one thousandth of that for the unsaturated acid, or its first hydrogen in the case of a dibasic acid.

The term "synthetic condensation polymer" as used herein designates polymers which can be formed by polymerisation with elimination of small molecules such as HCl, H<sub>2</sub>O, NaCl, NH<sub>3</sub>, and the like. Among such polymers may be mentioned polyamides, polyureas, polyurethanes, polyesters, polyethers, polysulphonamides and copolymers of such materials. Of particular interest are the linear polyamides which are prepared from polymerisable mono-amino carboxylic acids or their amide-forming derivatives, or from suitable diamines and suitable dicarboxylic acids or amide-forming derivatives of these compounds, especially polyamides having at least one aliphatic —HCR— group in each repeating unit of the polymer molecule, —R— being —O—, hydrogen, halogen or other monovalent atom or radical. The production of such polyamides is illustrated in Specification No. 461,236 and United States Specifications Nos. 2,071,250 and 2,130,948.

The term "ionising radiation" denotes radiation which has at least sufficient energy to produce ions or break chemical bonds, and includes radiation both in the form sometimes regarded as particle radiation and in the form sometimes regarded as ionising electromagnetic radiation. Although both types of radiation produce somewhat similar effects in some cases, the conditions of irradiation vary widely, so that each type has its specific utility.

The term "ionising particle radiation" denotes an emission of highly accelerated electrons or nuclear particles such as protons, neutrons, alpha-particles, or deuterons or beta particles directed so that the said particles impinge upon the polymer or article to be treated. The charged particles may be accelerated to high speeds by means of a suitable voltage gradient, using such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, a synchrotron, or cyclotron, as is well known to those skilled in the art. Neutron radiation may be produced by bombardment of selected light metal (e.g. beryllium) targets with high energy positive particles. In addition, suitable particle radiation may be obtained from an atomic pile, or from radioactive isotopes or other natural or artificial radioactive materials.

Ionising particle radiation has special utility for treating the polymers or articles which are thin or in thin layers. The required irradiation doses with present-day equipment are attained rapidly, in a matter of minutes, thus giving a high rate of throughput.

By "ionising electromagnetic radiation" is meant radiation such as is produced when a metal target (e.g. tungsten) is bombarded by electrons possessing appropriate energy. Such energy is imparted to electrons by accelerating potentials in excess of 0.1, preferably 0.5, million electron volts (Mev). Such radiation, conventionally termed X-ray, will have a short wave length, not more than about 0.01 Ang-

strom units with 1 Mev. electrons, and a spectral distribution of energy at longer wave lengths determined by the target material and the applied voltage. X-rays of wave lengths longer than 1 or 2 Angstrom units are attenuated in air and this places a practical upper limit on the wave length by the radiation. In addition to X-rays produced as indicated above, ionising electromagnetic radiation suitable for carrying out the process of the invention may be obtained from a nuclear reactor ("pile") or from natural or artificial radioactive material, for example cobalt 60. In these latter cases the radiation is conventionally termed gamma rays. Whilst gamma radiation is formally distinguished from X-radiation by reference to its origin, it may be noted that the spectral distribution of X-rays is different from that of gamma rays, the latter frequently being essentially monochromatic, which is never the case with X-rays produced by electron bombardment of a target.

Ionising electromagnetic radiation in the preferred wave lengths is highly penetrating, so that it readily lends itself to treating massive substrates. In the present invention this type of radiation is particularly useful for treating materials present in multiple layers of thin substrates. For example rolls of films, bolts of fabric, yarn packages and bales of staple fibres can be irradiated as a single unit. A method whereby rolls of material can be continuously irradiated is described and claimed in our Specification No. 798,340.

Although the treatment can be carried out using conventional X-ray equipment, the use of radioactive isotopes such as cobalt 60 is especially economical. Radiation from waste fission products, with particle irradiation screened off is desired, is also effective and offers an opportunity to utilise an otherwise useless waste product.

It will usually be desirable that high energy particles should have a velocity sufficiently high to permit penetration of several layers of fabric or film. The velocity required will depend on the nature of the particle and also on the nature of the substrate to a certain extent. An electron particle which is under acceleration by a potential of a million volts (Mev.) will effectively penetrate a thickness of polyhexamethylene adipamide of about 0.25 cm. regardless of the form of the shaped article, e.g. the nature of the weave of a fabric, the filament denier, and whether the shaped article is solid or a fabric formed from filamentary materials. Electrons of energy 2 Mev. will effectively penetrate a shaped article having a thickness of 0.5 cm. When surface effects are paramount, it is not necessary that the shaped article be completely penetrated by the high energy particle and lower accelerations may be employed, though if the surface effect is desired on both sides of the shaped article, it will obviously then be necessary to expose each side to the particle

radiation, either by simultaneously bombarding both sides of the shaped article or by subjecting each side to irradiation in turn, e.g. during successive runs past a single source of radiation.

5 Similarly when using ionising electromagnetic irradiation, it is desirable that the samples to be irradiated absorb as great a proportion of the incident radiation as possible. Since X- and especially gamma rays of short wave length  
10 are highly penetrating, it is often advantageous to combine a large number of thin samples into a relatively thick pile, and irradiate them simultaneously, thus utilising the machine time more efficiently. For example, when using X-  
15 rays generated by electrons of 2 Mev. the penetration is adequate for samples above 1.3 cm. thick. Lower energy (longer wave length) X-rays are of course less penetrating so that in such case it may be necessary to reduce the  
20 thickness of material which is to be treated simultaneously. Very long (soft) X-rays may be especially effective in producing surface effects, on account of their low penetrating power.

25 Radiation dosages from ionising "particles" (e.g. electrons) can be expressed as "Mrep" units (millions of roentgen equivalents physical), a "rep" being the amount of high energy particle radiation which results in an energy absorption of 83.8 ergs per gram of water or  
30 equivalent absorbing material; alternatively and perhaps more accurately, they are given in terms of radiation exposure in watt-seconds per square centimetre.

35 Dosages of ionising electromagnetic radiation (e.g. X-rays) may be expressed as "Mr" units (millions of roentgen), a roentgen being the amount of electromagnetic radiation which when absorbed in 1 cc. of dry air at standard  
40 temperature and pressure will produce 1 electrostatic unit of charge of either sign.

In determining the optimum dose of irradiation for any particular combination, both the nature of the organic compound and the nature of the solid substrate must be considered. When  
45 employing particle radiation in general, a dose of about 2 Mrep is adequate to initiate the bonding between the organic compound and the substrate, though it is preferred to use a dosage of at least about 8 Mrep. Higher  
50 dosages may be used and are frequently highly beneficial. Dosages so high that substantial degradation of the shaped substrate occurs must obviously be avoided. As a guide in this regard, fibres produced from polyhexamethylene adip-  
55 amide and polyethylene terephthalate may be irradiated to a dosage as high as 80 Mrep. However, it is preferred that the dosage applied to these substrates should not exceed about 60 Mrep.

60 Similarly, the same numerical doses, (expressed in Mr) are satisfactory when electromagnetic radiation is employed, although the exposure time with any given equipment is much greater (i.e. of the order of hours rather  
65 than minutes).

At constant temperature the degree to which the substrate is modified will depend upon the nature of the substrate, the nature of the modifier, the irradiation dose, and the concentration of the modifier on or in the substrate. In  
70 general the modifiers are applied to the substrate as liquids or solutions, preferably of relatively high concentration. Such procedure provides the maximum opportunity for the modifier to be exposed to the ionising irradiation.

75 A particular advantage possessed by textile articles and films and other shaped articles comprising the graft copolymers of the invention especially those in which the substrate is a polyamide, lies in their increased resistance to melting. Other advantages include increased resistance to flash heat, higher zero strength temperature and a high and unexpected degree of elasticity and deformability at high temperatures, for example above 185°C.; thus a  
80 polyamide fabric, after being treated, may be given a three-dimensional shape at high temperatures (e.g. by forming or embossing) without fusing of the individual filaments and without deleterious effect on the fabric hand, which  
90 shape is retained on cooling. When reheated above about 185°C., the fabric returns substantially to its original shape. Treated yarns may be elongated (drawn) at temperatures of 185°C. or above, whereby they acquire new  
95 tensile properties.

Alternatively, if a treated polyamide fibre is left free to retract when heated to temperatures of 185°C. or above, shrinkages of 50% or more are observed. This property permits  
100 textured effects to be obtained when treated and untreated yarns are combined in the same fabric, or when the unsaturated acid or the metal ions are applied in a pattern (i.e. non-uniformly), or indeed when portions of the  
105 shaped substrate are shielded from the irradiation.

It has also been found that the elastic modulus (at 25°C.) of a polyamide treated in accordance with this invention is substantially  
110 increased, especially when the polyamide is held under tension during irradiation.

The invention is illustrated by the following Examples.

#### EXAMPLE I

115 A swatch of 66 nylon fabric (taffeta weave, woven from 70 denier 35 filament yarn) is padded to saturation with a solution of 25 g. of maleic anhydride dissolved in 75 g. of water, wrapped in aluminium foil and passed 40 times  
120 under an electron beam from a Van de Graaff electron accelerator using a Van de Graaff generator. The total exposure is 40 Mrep. or 500 watt-sec./cm<sup>2</sup>. The treated fabric is removed from the aluminium foil and agitated  
125 for 2 hours in a 20 litre washing machine containing distilled water at 70°C. to remove unreacted maleic anhydride. The weight gain of the fabric after drying is 8%. If either the padding with maleic anhydride or the irradiation  
130

tion step is omitted, then no weight gain is observed.

The maleic acid-modified nylon is next after-treated by agitation for 2 hours in a 20 litre washing machine containing 20 g. of "Tide" (Registered Trade Mark) detergent (which contains basic metallic salt as shown hereinbefore) dissolved in 18 litres of distilled water at 70°C. It is then thoroughly rinsed in distilled water and dried. An additional weight gain of 7% is noted. When hot ashes from a burning cigarette are flicked onto the fabric to determine its hole-melting tendency, only a small brown stain results. Holes are immediately melted through a fabric which has not been treated with the unsaturated acid and the metallic ions, whether irradiated or not. The hole-melting tendency of the fabric is measured quantitatively by dropping heated glass beads of constant weight and diameter from a fixed height from a constant temperature oven onto the fabric. The temperature at which the fabric is stained is called the first damage temperature, and the temperature at which the glass bead melts completely through the fabric is referred to as the hole-melting temperature. The fabric treated according to this Example has a first damage temperature of 300°C., compared with 275°C. for an untreated control, and a hole-melting temperature of 600°C., compared with 310°C. for an untreated control. The fabric has elastomer properties such that when heated above 185°C. it can be formed and drawn to as much as 3 times its room temperature length. In addition the fabric is observed to have been delustered, as is shown by reduction in the percentage of incident light transmitted from an original value of 1.5% to 0.5%. Furthermore the texture is changed so that it has a much drier handle than the untreated control. The treated fabric is soluble in 90% formic acid, but is insoluble in hot *m*-cresol. The original nylon is soluble in both solvents.

When the fabric modified in accordance with the Example is stirred for one hour at 70°C. in a beaker containing 190 ml. of distilled water and 10 grams glacial acetic acid (which removes metallic ions from the fabric), the fabric loses its high temperature properties. Furthermore its hole-melting resistance is reduced to that of an untreated control and it is now

soluble in hot *m*-cresol. Its resistance to hole-melting is restored by a second washing treatment in the "Tide" detergent solution, and the fabric is again insoluble in hot *m*-cresol. When 0.1 normal hydrochloric acid is substituted for the 5% acetic acid, and the test repeated, similar results are obtained; thus the fabric shows the properties of an ion exchange resin.

#### EXAMPLE II

It is sometimes desirable to treat a nylon fabric with an unsaturated acid or acid anhydride and also with another modifying agent. For example, a sample of 66 nylon fabric is immersed in a mixture of 30 parts maleic anhydride, 70 parts methoxydecaethyleneoxy methacrylate monomer and 100 parts of water. The sample is wrung out, wrapped in aluminium foil and irradiated to a total dosage of 20 Mrep. (125 watt-sec./cm<sup>2</sup>.) using the equipment and technique of Example I. The fabric is then subjected to 15 standard washings using a detergent containing sodium ions as disclosed above. It is observed to have a much drier hand than an irradiated comparative control which was not immersed in the liquid mixture prior to irradiation. Hot ashes from a burning cigarette are flicked onto the treated fabric to determine its hole-melting tendency. Only a small brown stain results. Holes are immediately melted through the original fabric, whether irradiated or not.

When the above experiment is repeated employing fabric made from polycapromamide yarn, similar results are obtained.

#### EXAMPLE III

A portion of the nylon fabric of Example II is immersed in a 25% solution of maleic anhydride, the excess liquid squeezed from it, the sample enclosed in aluminium foil and irradiated under the conditions of Example I. The irradiation exposure is 40 passes (40 Mrep.) or 500 watt-sec./cm<sup>2</sup>. After irradiation the sample is cut into 6 pieces marked AQ to AV inclusive. The pieces, except for Sample AV, are washed in an agitation washer using water at 70°C. with or without additions as indicated in Table I. After being washed the samples are rinsed, dried and tested to determine their resistance to hole-melting, with the results indicated in Table I. Sample AV is a control which was subjected to all the treatments outlined above except irradiation.

TABLE I

Sample	Wash Composition	No. of Washings	Resistance to Hole-Melting
AQ	20 grams "Tide", 18 litres of tap water	2	Excellent
*AR	20 grams "Tide", 18 litres of tap water	2	Fair
AS	18 litres of tap water	1	Good
AT	18 litres distilled water	1	Poor
AU	13 grams of $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ 18 litres tap water	1	Excellent
AV	(No washing)	None	Poor
AW	20 grams "Tide", 18 litres tap water	2	Poor

\* No agitation used.

"Tide" is a Registered Trade Mark.

The tap water used in the washing contains approximately 11 parts per million of calcium ion.

- 5 The results obtained in this Example show that substantial resistance to hole-melting is produced when the nylon fabric with the maleic anhydride grafted thereon is exposed to metal ions present in the "Tide" solution, in the hard tap water, or in the solution containing sodium phosphate. It is also apparent that a material improvement in the treatment is obtained when the treatment is carried out under conditions of agitation.

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#### EXAMPLE IV

Portions of the fabric of Example II are immersed in 25% aqueous maleic anhydride,

then irradiated under the conditions of Example III. The irradiated fabric is divided into sections and treated as shown in Table II. Sample swatches AX to BC are subjected to 40 passes under the Van de Graaff electron accelerator for a total exposure of 500 watt-sec./cm<sup>2</sup>, and samples BD to BF inclusive are given an exposure of 80 passes for a total exposure of 1000 watt-sec./cm<sup>2</sup>. Each of the irradiated samples identified by letter is then agitated for 1 hour in a washing machine containing 18 litres of distilled water at 70°C. and 20 grams of the indicated salt, as shown in Table II. The samples are then rinsed in hot distilled water, dried and tested for resistance to hole-melting.

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TABLE II

Sample	Salt in Treating Solution	Resistance to Hole-Melting
AX	Sodium carbonate	Excellent
AY	Potassium carbonate	Excellent
AZ	Potassium acetate	Good
BA	Calcium acetate	Excellent
BB	Manganous acetate	Excellent
BC	Zinc acetate	Excellent
BD	Cupric acetate	Good
BE	Cobaltous acetate	Excellent
BF	Chromic acetate	Good

Sample BD (with cupric ion attached) is light green in colour,  
BE (with the cobaltous ion) is light pink.

From the above results it is apparent that a substantial improvement in resistance to hole-melting has been attained by treatment of the irradiated, maleic anhydride-grafted nylon fabric with a variety of positively charged metallic ions.

#### EXAMPLE V

The effect of the acid strength of the anion of the metal salt is shown in this Example. Three nylon fabric samples coded, BG, BH, BI, are immersed in maleic anhydride solution and irradiated to the same exposure as sample

BD of Example IV. Each is then immersed in a solution containing 10 parts of one of the salts shown in Table III, in 100 parts of water. The samples and salt solutions are boiled for 30 minutes, rinsed in hot distilled water, dried and tested for resistance to hole-melting, with the results shown in Table III. Also listed in Table III is the anion of the metal salt, and the dissociation constant for the reaction whereby that anion is produced from its parent acid.

TABLE III

Sample	Salt	Anion	Dissociation Constant*	Resistance to Hole Melting
BG	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	$\text{H}_2\text{PO}_4^-$	$1.1 \times 10^{-2}$	Poor
BH	$\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	$\text{HPO}_4^{2-}$	$7.5 \times 10^{-8}$	Good
BI	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	$\text{PO}_4^{3-}$	$4.8 \times 10^{-13}$	Good

\* Handbook of Chem. & Phys., 34 Ed., P. 1560 (Chem. Rubber Pub. Co. Cleveland — 1952).

The dissociation constant of the maleic acid grafted to the polyamide is  $1.5 \times 10^{-2}$  for the first hydrogen and  $2.6 \times 10^{-7}$  for the second. There is thus little effect in producing resistance to hole melting on exposing sample BG to a solution of about the same acid strength as the attached organic acid. Good results are obtained when metal salts with weaker acid anions are used.

Similarly, good resistance to hole melting is attained when a nylon sample treated like AX

of Example IV is treated with a sodium hydroxide solution, but no improvement results when the sodium hydroxide is replaced by sodium chloride.

It also is to be noted that in Example IV, sample AY, treated with potassium carbonate (acid dissociation constant  $3.5 \times 10^{-7}$ ) gives better resistance to hole melting than Sample AZ, treated with potassium acetate (acid dissociation constant  $1.75 \times 10^{-5}$ ).

## EXAMPLE VI

5 Nine samples of the nylon fabric of Example II are immersed in solutions of grafting agents as shown in Table IV. The excess of the reagent is squeezed from the fabric. Each sample is enclosed in an aluminium foil wrapper and thereafter irradiated in the equip-

ment and under the conditions of Example III, with the exposures shown in Table. After 10 standard washings in "Tide" detergent and 48 hours extraction in a Soxhlet extractor with acetone, the per cent weight gain is determined, as well as the resistance to hole-melting.

TABLE IV

Sample	Grafting Agent	Concentration Applied	Total Exposure Watt-sec./cm. <sup>2</sup>	Weight Gain (%)	Resistance to Hole Melting
BJ	dichloro-	25% in H <sub>2</sub> O	500	(not measured)	Excellent
BK	maleic anhydride	25% in H <sub>2</sub> O	1000	20	Excellent
BL	maleic acid	Satd. soln. in H <sub>2</sub> O	500	14	Excellent
BM	fumaric acid	Satd. soln. in H <sub>2</sub> O	1000	39	Excellent
BN	itaconic acid	25% in ethanol	500	11	Good
BO	crotonic acid	24% in H <sub>2</sub> O	1000	14	Good
BP	furoic acid	Satd. soln. in H <sub>2</sub> O	1000	9	Good
BQ	acrylic acid	25% in H <sub>2</sub> O	1000	32	Fair
BR	succinic acid	Satd. soln. in H <sub>2</sub> O	500	(not measured)	Poor

15 In the next Example X-radiation is employed. The samples are exposed to the X-radiation using a resonant transformer X-ray machine marketed by the General Electric Co., Schenectady, New York, known as a "Two  
20 Million volt Mobile X-ray Unit." This machine is described by E. E. Charlton and W. F. Westendorf in the Proceedings of the First National Electronics Conference, p. 425, October 1944. The pile of packaged samples is  
25 placed in an open top box made from  $\frac{1}{16}$  inch sheet lead, and positioned so that the top sample is 8 cm. from the tungsten tube target. At this location, using a tube voltage of 2 Mev, and a tube current of 1.5 milliamperes, the  
30 irradiation rate is 1.5 Mr per hour. The beam irradiates a circle about 3 inches in diameter; all fabric tests are made on the irradiated portion.

## EXAMPLE VII

35 Samples of 66 nylon fabric are exposed to X-radiation to a total dose of 27 Mrep as described above, after immersion in a mixture of 30 parts maleic anhydride, 70 parts of methoxydodecaethyleneoxy methacrylate mono-  
40 mer and 100 parts water. The fabric is then subjected to 15 standard washings using a detergent which contains basic-reacting metallic

salt. The final fabric is observed to have a dryer hand than an irradiated comparative control which is not immersed in the liquid mixture prior to irradiation. Hot ashes from a burning cigarette are flicked onto the liquid-immersed, irradiated, washed fabric to determine its "hole-melting" tendency. Only a small brown stain results. Holes are immediately melted through the untreated fabric, whether irradiated or not. A treated sample irradiated with a dose of only 13.5 Mr gives a smaller degree of resistance to hole melting. A treated sample which has not been irradiated shows no improvement in resistance to hole-melting after 5 washings. The properties of the fabric are similar in other respects to those obtained in Example II.

## EXAMPLE VIII

60 Samples of 66 nylon (BS to BX inclusive) and 6 nylon (polyamide from caprolactam) fabric (BY and BZ), prepared from 70 denier, 34 filament yarn, are cut into 8" x 1" strips, soaked in various unsaturated acids as shown  
65 in Table V, and then folded into 1" x 1" squares which are individually wrapped in aluminium foil, and are then exposed to X-radiation produced from a 2-million electron volt (2 Mev) Van de Graaff electron accelerator  
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operated so that the electrons impinge on a gold target, generating X-rays which are directed onto the pile of samples. The distance of sample to tube window is 2 centimetres.

5 Tube voltage is 2 Mev, the current is 250 micro-amperes, and the radiation dosage is about 2 Mrep per hour.

After irradiation for a period of 8 hours, giving an exposure of about 15 Mr, the fabric

10 samples are removed and washed in distilled water at about 70°C., with vigorous agitation, for several half-hour periods. The samples are then dried and weighed. The weight gain of each is shown in Table V. The fabrics are then

15 treated with various metallic salts dissolved in

water at 70°C., with rapid agitation, covering several 1-hour periods. The samples are then rinsed thoroughly in distilled water, dried, weighed, and tested for heat resistance.

The maleic anhydride and maleic acid are applied to the polymer substrate as a 25% solution in water. The itaconic and fumaric acids are applied as saturated aqueous solutions. The calcium acetate solution used in the post-treatment step consists of 50 grams of calcium acetate dissolved in 5 litres of distilled water. The trisodium phosphate solution consists of 10 grams of trisodium phosphate dissolved in 5 litres of distilled water. The results of these experiments are as indicated.

TABLE V

Sample	Unstaturated Acid	Wt. Gain %	Metallic Salt	Additional Wt. Gain %	Resistance to Hole-Melting
BS	Maleic anhydride	9.2	$\text{Ca}(\text{CH}_3\text{COO})_2$	3.5	Excellent
BT	Maleic anhydride	9.2	$\text{Na}_3\text{PO}_4$	0.5	Excellent
BU	Itaconic Acid	9.2	$\text{Ca}(\text{CH}_3\text{COO})_2$	2.4	Excellent
BV	Itaconic Acid	9.2	$\text{Na}_3\text{PO}_4$	0.5	Excellent
BW	Fumaric Acid	8.0	$\text{Ca}(\text{CH}_3\text{COO})_2$	2.6	Excellent
BX	Fumaric Acid	8.0	$\text{Na}_3\text{PO}_4$	Not measurable	Excellent
BY	Maleic Acid	6.8	$\text{Ca}(\text{CH}_3\text{COO})_2$	2.9	Excellent
BZ	Maleic Acid	6.8	$\text{Na}_3\text{PO}_4$	0.8	Good

Conventionally drawn polyamide yarn when treated in accord with this invention becomes highly darwable at elevated temperatures (e.g. above 185°C.), as compared to the untreated yarn, as shown below.

## EXAMPLE IX

66 Nylon yarn of 34 filaments is drawn to 5.17 times its as-spun length as described in Specification No. 543,466. The yarn has a denier of about 220. To prevent entanglement during washing, it is woven into a fabric having a polyethylene terephthalate warp. Three samples of the fabric are soaked in a 25% aqueous solution of maleic acid. Three of these, CA, CB and CC are irradiated under the conditions of Example I. Sample CC is a control. A dose of 20 Mrep is used. Sample fabrics CA, CB and CC are then thoroughly rinsed in distilled water to remove excess acid. Thereafter CA and CB are agitated for several 30-minute periods in a 20 litre washing machine containing 18 litres of distilled water at 70°C. and 20 grams of calcium acetate. The fabrics are again rinsed in distilled water to remove unreacted ions, dried, and the nylon yarn un-

ravelled and then backwound onto cones. The treated irradiated yarn is then post drawn at a feed rate of 7 feet per minute over a hot pin at 160°C. and a hot surface at 250°C., using the apparatus of Hume (United States Specification No. 2,533,013). Yarn of fabric CA is drawn 2.1 times and CB is drawn 2.6 times its original length. Control CC fuses and breaks immediately, when attempts are made to draw it. Two other controls, neither of which is soaked in maleic anhydride, but each of which is washed (CD being irradiated and CE being not irradiated) also break and fuse when attempts are made to draw them.

Similar results are obtained on repeating the foregoing Example, using electromagnetic irradiation (as in Example VIII) instead of particle irradiation.

For improving the properties of polyamides at elevated temperatures, the positively charged metallic ions are most effective. However, when high temperature effects are not paramount, other positively charged ions (e.g. ammonium) may be reacted with the organic acid modified nylon to produce changes in hand, static

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properties, lustre or colour, or other effects.

Specification No. 758,735 claims a process for improving the crocking and colour-fastness properties of pigment-printed surfaces of textile and other fibrous material in which the pigmented printing composition with which the textile or other fibrous material has been printed comprises a pigment, a resinous or cellulose derivative carrying agent, and a binder for the pigment selected from (1) electron activatable monomeric polymerisable compounds, (2) electron activatable polymeric compounds and (3) mixtures of electron activatable monomeric polymerisable compounds and polymeric compounds, which process comprises subjecting the pigment-printed material to irradiation with high energy electrons, whereby the binder is converted to a product of higher molecular weight. This subject matter is not here claimed.

Subject to the foregoing disclaimer, WHAT WE CLAIM IS:—

1. Graft copolymers in which the substrate is a synthetic condensation polymer and the grafted structures at least in part contain free carboxyl groups or carboxylate salt groups and are derived from monomers containing reactive non-aromatic carbon-carbon unsaturation.

2. Graft copolymers according to claim 1, wherein the acid grafted structures are in the form of metal salts of the unsaturated carboxylic acids.

3. Graft copolymers according to claim 1 or 2, wherein the grafted structures are derived from ethylenically unsaturated acids containing up to 5 carbon atoms in the molecule.

4. Graft copolymers according to claim 3, wherein the unsaturated acid is acrylic, crotonic or furoic acid.

5. Graft copolymers according to any of claims 1—3, wherein the grafted structures are derived from an unsaturated dibasic acid.

6. Graft copolymers according to claim 5, wherein the unsaturated acid is maleic, dichloromaleic, fumaric or itaconic acid.

7. Graft copolymers according to any of the preceding claims, wherein the synthetic condensation polymer is a polyamide.

8. Graft copolymers according to claim 7, wherein the polyamide is polyhexamethylene adipamide or poly- $\epsilon$ -caproamide.

9. Graft copolymers according to claim 1 substantially as hereinbefore described.

10. Textile articles, films and other shaped articles comprising a graft copolymer claimed in any of claims 1—9.

11. Textile articles according to claim 10 substantially as described in the foregoing Examples.

12. Process for the production of a graft copolymer claimed in any of claims 1—9, which comprises subjecting the synthetic condensation

polymer to ionising radiation while it is in intimate contact with a modifier consisting of the corresponding unsaturated acid or an anhydride, half-acid ester or half-acid amide thereof, or a derivative thereof than can be, and subsequently is, hydrolysed to the acid.

13. Process according to claim 12, wherein the synthetic condensation polymer is in the form of a shaped article.

14. Process according to claim 13, wherein the polymer is in the form of a textile fabric or other textile article or a film.

15. Process according to claim 13 or 14, wherein the modifier is applied to the surface of the shaped article.

16. Process according to any of claims 13—15, wherein the surface layers only of the shaped article are subjected to the action of the ionising radiation.

17. Process according to any of claims 13—16, wherein a number of layers of textile materials or films or foils are simultaneously subjected to the action of X-rays or gamma rays of short wavelengths.

18. Process according to any of claims 12—17, wherein the modifier is dispersed in or diffused into the condensation polymer.

19. Process according to any of claims 12—18, wherein the condensation polymer or shaped article thereof is kept in an inert atmosphere while it is irradiated.

20. Process according to any of claims 12—19, wherein the condensation polymer or shaped article thereof is enclosed by a polyethylene film or aluminium foil or other material which is impervious to air and water while it is irradiated.

21. Process according to any of claims 12—20, wherein the condensation polymer or shaped article thereof contains or is in contact with a compound having a protective or anti-oxidant effect with respect to the polymer or the modifier or both.

22. Process according to any of claims 12—21, wherein calcium tungstate, zinc sulphide, metallic lead, or other radiation transfer agent capable of absorbing radiation and re-emitting it in a form of lower energy is present during the irradiation.

23. Process according to any of claims 12—22, wherein the temperature of the condensation polymer or shaped article thereof during the irradiation is kept between 0° and 75°C., if necessary by cooling it.

24. Process according to any of claims 12—23, wherein the graft copolymer so obtained is subjected to the action of a solution containing a metal salt of an acid which is weaker than the grafted unsaturated acid (first hydrogen in the case of a dicarboxylic acid).

25. Process for the production of a graft copolymer in the form of a fabric and in

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